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(54) TRANSPARENT BLACK ELECTROCONDUCIVE FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To impart low reflecting, high contrast and electromagnetic wave shielding properties to a transparent black electroconductive film by forming a lower layer containing a metallic fine powder and a black powder and a siliceous upper layer on the lower layer in a siliceous matrix on the surface of a transparent substrate.

SOLUTION: This transparent black electroconductive film is a two-layer film composed of a lower layer containing an electroconductive powder in a siliceous matrix and a siliceous upper layer free of the powder. Since the lower layer is an electroconductive layer densely containing the powder, the refractive index thereof is high, whereas the upper layer has a low refractive index. When an electroconductive film having the two-layer film constitution is formed on the glass surface of a cathode-ray tube front panel, the following effects are obtained: The leakage of electromagnetic waves, sticking of dust and reflecting in of an external image deteriorating the visibility are prevented or reduced while maintaining the color tone of an image good. The contrast of the image is raised and the haze is good without darkening the image to a greater extent than that is necessary.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the transparence black nature electric conduction film of high contrast nature by the low reflexibility suitable for giving functions, such as prevention electrification prevention, electromagnetic wave shielding, and reflected, to transparence bases, such as the Braun tube.
[0002]
[Description of the Prior Art] Dust tends to adhere with static electricity, and since a front face is high reflexibility, the trouble that an image becomes not clear by reflection of the light of the exterior to a screen or reflected [an external image] is shown in the front face of the front panel glass which is the image display section of the Braun tube containing TV or various CRT for a display. Moreover, recently, we come to be anxious about the effect to the body of the electromagnetic wave which comes out of the Braun tube, and the specification over the leakage electromagnetic wave of low frequency has also come to be enacted in each country.
[0003] Generally a means to form the transparence electric conduction film with the antistatic effectiveness or an electromagnetic wave shielding effect in an offscreen side has been adopted as antisticking of dust, or the leakage control of an electromagnetic wave. Generally non-glare processing over which detailed irregularity processing of the glass front face of a screen is carried out, using fluoric acid etc. as reflected preventive measures, and light is scattered has been performed. However, non-glare processing worsens the resolution of an image and has the problem that visibility falls.
[0004] Therefore, recently, to be reflected with antistatic (dust antisticking) and to give the function of both prevention on the transparence electric conduction film of a high refractive index, with the two-layer film in which the transparence overcoat film of a low refractive index was formed, is tried. By such two-layer film, if the refractive-index difference of the high refractive-index film and a low refractive index film is large, the reflected light from the upper low refractive index film front face will be negated by interference of the reflected light from an interface with the lower layer high refractive-index film, and reflected will be prevented as a result. When the conductivity of this transparence electric conduction film is high, an electromagnetic wave shielding effect is also given to coincidence.
[0005] for example, to JP,5-290634,A Sb dope tin oxide (ATO) Apply to a glass base the alcoholic dispersion liquid which distributed impalpable powder using the surfactant, and it dries. The conventional conductive refractive index (1.50-1.54) High refractive index (1.55-2.0) The electric conduction film which it had is formed. It is magnesium fluoride on it. (1.38) Silica formed from the alkoxysilane which may be contained (1.45) By forming a low refractive index film, the two-layer film which reduced the reflection factor to 0.7 % is proposed.
[0006] the optical thickness nd (n: thickness, d:refractive index) of the high refractive-index layer-low refractive-index layer formed on the base at JP,6-12920,A -- respectively -- 1/2lambda-1/4lambda (wavelength of lambda= incident light) ** -- when it carries out, becoming low reflexibility is indicated. According to this official report, a high refractive-index layer is ATO or Sn dope indium oxide. (ITO) It is the film of the quality of a silica containing impalpable powder, and a low refractive-index layer is the silica film.
[0007] The two-layer film which also becomes JP,6-234552,A from an ITO content silicate quantity

refractive-index electric conduction film-silicate glass low refractive index film is indicated. The two-layer film of the high refractive-index electric conduction film and low refractive index film which applied and formed conductive impalpable powder and the liquid containing Ti salt in JP,5-107403,A is indicated.

[0008] JP,6-344489,A -- ATO impalpable powder and black conductivity impalpable powder (preferably carbon black impalpable powder) from -- the two-layer film which consists of the 1st becoming layer membrane of a high refractive index with which solid content was filled up densely, and a low refractive index film of the quality of a silica formed on it and which wore the black taste is indicated.

[0009]

[Problem(s) to be Solved by the Invention] However, by the transparence electric conduction film which used the conductive powder of ATO or semi-conductor nature called ITO, it is difficult to form low resistance so that an electromagnetic wave shielding effect may be produced, or even if it can carry out [low ****]-izing so that an electromagnetic wave shielding effect may be produced, thereby, transparency is checked remarkably. Recently, specification [especially as opposed to the leakage electromagnetic wave from the Braun tube] becomes severer, the conventional technique of an electromagnetic wave shielding effect mentioned above is inadequate, correspondence is difficult, and the large transparence electric conduction film of an electromagnetic wave shielding effect is called for more by low resistance.

[0010] The purpose of this invention is offering the transparence black nature electric conduction film which was formed into low resistance so that the electromagnetic wave shielding effect of a high level might be demonstrated, held the transparency and the low haze value which moreover do not check the visibility of the Braun tube, and was equipped with the low reflexibility which can give the reflected prevention function of high contrast and an external image to the Braun tube.

[0011]

[Means for Solving the Problem] If this invention persons take into consideration the latest severe specification over electromagnetic wave shielding [of the Braun tube] As conductive powder used for the transparence electric conduction film, it is not the non-subtlety powder of ATO or semi-conductor nature called ITO. As a result of reaching a conclusion that use of metal impalpable powder with more high conductivity is desirable and advancing examination further, it found out that the above-mentioned purpose could be attained with the two-layer film which prepared the upper coat of a low refractive index of the quality of a silica in the lower layer transparence electric conduction film containing metal impalpable powder and black powder.

[0012] It is the equipped with low reflexibility and quantity KONSUTO last nature, and electromagnetic wave shielding transparence black [here] nature electric conduction film. [which this invention becomes from the lower layer which contains metal impalpable powder and black powder in the nature matrix of a silica prepared in the front face of a transparence base, and the upper layer of the quality of a silica prepared on it] If it is in a suitable mode, the above-mentioned black powder is black titanium oxide, and the above-mentioned transparence base is the image display section of the Braun tube.

[0013]

[Embodiment of the Invention] It is good at the transparence base of arbitration with desirable especially the transparence base that forms the transparence black nature electric conduction film of this invention not being restricted, but giving low reflexibility and electromagnetic wave shielding. Although a typical transparence base is glass, the transparence black nature electric conduction film of this invention can also be formed on bases, such as a transparent plastic.

[0014] As mentioned above, the transparence base with which especially low reflexibility and electromagnetic wave shielding grant is called for is the front panel of the Braun tube used as indicating equipments, such as TV and a computer. The transparence black nature electric conduction film of this invention is low reflexibility and electromagnetic wave shielding (low resistance). In addition, it has the description that contrast nature is high. Therefore, if this electric conduction film is formed in the glass front face of the Braun-tube front panel, it can be harmful to health, reflected [to which the cause of malfunction of a computer worsens visibility with leakage of an electromagnetic wave and adhesion of dust] can be prevented thru/or reduced, holding the color tone of an image good, and contrast of an image can be made high. Moreover, a haze is also good and an image is not made dark beyond the need.

[0015] The transparence black nature electric conduction film of this invention is two-layer film which consists of a lower layer which contains conductive powder in the nature matrix of a silica, and the upper layer of the quality of a silica which does not contain powder. Since a lower layer is a conductive layer which contains metal impalpable powder and black powder densely, the upper layer is a low refractive index to a thing with a high refractive index. By this two-layer film configuration, the transparence black nature electric conduction film of this invention has the property of low reflexibility, low resistance, and high conte lath nature, and can demonstrate the above-mentioned function.
[0016] the transparence black nature electric conduction film of this invention -- setting -- the nature matrix of a silica of a lower layer conductive layer, and the upper layer of the quality of a silica -- each -- alkoxysilane (a wide sense hydrolysis nature silane compound) from -- it can form.
[0017] As alkoxysilane, one sort or two sorts or more of at least one silane compound [two or more] of the arbitration which has three or more alkoxyl groups still more preferably can be used preferably. It can be used together with alkoxysilane, being able to replace with alkoxysilane the halo silanes which contain a halogen as a radical of hydrolysis nature.
[0018] as the example of alkoxysilane -- tetra-ethoxy silane (= ethyl silicate) Tetra-propoxysilane, methyl triethoxysilane, dimethyldimethoxysilane, phenyltriethoxysilane, KURORU trimethoxysilane, and various kinds of silane coupling agents (an example --) Vinyltriethoxysilane, gamma-aminopropyl triethoxysilane, Gamma-chloropropyltrimetoxysilane, gamma-mercapto propyltrimethoxysilane, Gamma-glycidoxypropyltrimetoxysilane, gamma-methacryloxpropyl trimethoxy silane, N-phenyl-gamma-aminopropyl trimethoxysilane and N-beta- (aminoethyl) -gamma-aminopropyl trimethoxysilane and beta-(3, 4-epoxycyclohexyl) ethyltrimethoxysilane etc. -- it is mentioned. The ethyl silicate which it is the cheapest and is hydrolyzed easily is desirable.
[0019] If hydrolysis is received, alcohol will ****, and the generated OH radicals will condense the coat which consists of alkoxysilane, and it will become a silica sol. When this sol is heated and baked, condensation progresses further and, finally it is a hard silica. (SiO2) It becomes a coat. Therefore, when alkoxysilane can be used for forming the nature coat of a silica as an inorganic coat formation agent and is coat-ized together with powder, it will function as an inorganic binder which combines powder, and will constitute the matrix of a coat. In addition, although a halo silane can finally form a silica coat similarly by hydrolysis, below, it explains as what uses alkoxysilane.
[0020] The lower layer conductive layer of the transparence black nature electric conduction film of lower layer conductive layer this invention contains metal impalpable powder and black powder in the nature matrix of a silica. The nature matrix of a silica can be formed from alkoxysilane, as mentioned above.
[0021] As metal impalpable powder, unless it has a bad influence on film-forming [of alkoxysilane], the mixture of the metal of arbitration, the powder of an alloy or a metal and/, or alloy powder can be used. The mixture of one sort or two sorts or more of metals chosen from the group which consists of Fe, Co, nickel, Cr, W, aluminum, In, Zn, Pb, Sb, Bi, Sn, Ce, Cd, Pd, Cu, Pt, Ag, and Au and/or the alloy of these metals and/or these metals and/, or an alloy is desirable as the quality of the material of metal impalpable powder. In these, especially desirable metal kinds are nickel, W, In, Zn, Sn, Pd, Cu, Pt, Ag, and Au, and Ag of low resistance is the most desirable. Although desirable alloys are silver alloys, such as Cu-Ag, nickel-Ag, Ag-Pd, Ag-Sn, and Ag-Pb, they are not limited to this. Moreover, the mixture of Ag and other metals (s, such as an example, and W, In, Sn, Pb, Cu, Bi) is also desirable as metal impalpable powder.
[0022] In metal impalpable powder, one sort of alkaline earth metal, such as alkali metal, such as one sort or two sorts or more of nonmetals, such as P, B, C, N, and S, or Na, K, and/, or Mg, calcium, or two sorts or more may be dissolving.
[0023] Let particle size of metal impalpable powder be the particle size which does not check the transparency of the electric conduction film. For desirable metal impalpable powder, at this semantics, the first [an average of] particle diameter is 0.1. It is a thing 0.05 micrometers or less more preferably below mum. The metal impalpable powder which has this mean particle diameter is the technique of colloid generation. (a metal is made to return metallic compounds with a suitable reducing agent under existence of an example and protective colloid) It can use and manufacture. Especially the particle shape of metal impalpable powder may not be restricted, but the shape of a globular shape, an irregular configuration, and flat and any needlelike any are sufficient as it.

[0024] As conductive powder, it adds to metal impalpable powder and is the transparent conductive impalpable powder of inorganic oxide systems, such as ITO and ATO. (the first [an average of] particle diameter is as follows [0.1 mum] preferably below 0.2 mum) It can also use together. Even in such a case, it is desirable to make it more than one half of conductive powder serve as metal impalpable powder.

[0025] Black powder is blended in order to give black nature to the transparence electric conduction film of this invention. Although the black powder which has conductivity is more desirable as black powder, since conductivity is fully given by the conductive high metal impalpable powder which lives together, in this invention, black powder may not have conductivity. Especially the first [an average of] particle diameter of black powder is 0.1 so that transparency may not be checked remarkably, although not restricted. The following [mum] are desirable.

[0026] As black powder with conductivity, black titanium oxide, graphite powder, magnetite powder (Fe 3O4), carbon black, etc. are mentioned. Especially, especially light absorptivity of black titanium oxide is the most desirable from a high thing. Black titanium oxide is the powder of acid titanium nitride with the presentation shown by TiOx-Ny ($0.7<x<2.0$, $y< 0.2$), and since an oxygen defect is in a crystal lattice, it shows conductivity. It sets to the above-mentioned presentation and especially desirable black titanium oxide is x. 0.8-1.2 It is a thing. AgO etc. is mentioned as black powder without conductivity.

[0027] The blending ratio of coal of metal impalpable powder and black powder is the weight ratio of metal impalpable powder:black powder, and it is desirable to consider as within the limits of 5:95-97:3. This weight ratio is 15:85-95:5 more preferably. As mentioned above, the transparent conductive powder of inorganic oxide systems, such as ATO and ITO, may be substituted for a part of this metal impalpable powder.

[0028] Since the amount of black powder increases when sufficient low resistance-ization for electromagnetic wave shielding reservation will become impossible, if there are too few amounts of metal impalpable powder, it is membranous transparency. (light permeability) It falls. if there are too few amounts of black powder -- spectral-reflectance curve of a visible region (reflectance spectrum) the short wavelength side seen and a long wave -- increase of the reflection factor by the side of merit becomes rapid, even if the low reflexibility below light minimum reflection factor 1.0 % made into the purpose is attained, the reflected light wears blue - purplish, or the red - yellow taste, and visibility is spoiled remarkably.

[0029] The amount of the nature matrix of a silica in a lower layer conductive layer should just be sufficient amount to combine metal impalpable powder and black powder. Since this conductive layer is covered with the upper layer of the quality of a silica, high film reinforcement or a high degree of hardness are not needed especially. Generally, 15 or less % of the weight may be enough as the amount of the nature matrix of a silica required for powdered association, and about 1% of the weight of small quantity is sufficient as it depending on the case. This amount is 5 - 10 % of the weight preferably.

[0030] The lower layer conductive layer which contains metal impalpable powder and black powder in the nature matrix of the formation approach silica of the transparence black nature electric conduction film Alkoxysilane (this may be made to hydrolyze beforehand) Into a solution, the coating which distributed metal impalpable powder and black powder is applied to the front face of a transparence base, is heated, and a paint film is baked. (alkoxysilane is made to convert into the quality of a silica) It can form by things. Then, if the coating which consists of a solution of the alkoxysilane for the upper formation is applied and heated, a paint film is baked and the upper nature coat of a silica is formed, the transparence black nature electric conduction film of the two-layer structure of this invention will be formed. Hereafter, let this approach be the 1st approach.

[0031] The coating which does not contain the alkoxysilane which functions as an inorganic binder as 2nd another approach, i.e., the coating which distributed metal impalpable powder and black powder in the solvent, can be used, and a lower layer conductive layer can also be formed. If this coating is applied to the front face of a transparence base, it dries and a solvent is evaporated, the powder coat from which it consists only of metal impalpable powder and black powder substantially, and the space between particles serves as an opening will be formed in a base front face excluding a matrix. Each of metal impalpable powder and black powder consists of a submicron particle, and since coherent is strong, even if a binder does not exist, it can carry out [coat]-izing.

[0032] Then, if the coating which consists of a solution of the alkoxysilane for the upper formation is

applied like the 1st approach, some applied solutions will permeate the opening between lower layer particles, and it will function as a binder which combines a particle. The solution which was not able to permeate into the lower layer coat performs spreading of the alkoxysilane solution at this time so that it may remain on a lower layer coat. Subsequently, if it heats, a coat is baked and alkoxysilane is made to convert into the quality of a silica, the alkoxysilane which permeated between lower layer particles serves as a nature matrix of a silica which fills the opening between particles, the alkoxysilane which was not able to permeate will form the upper nature coat of a silica, and the transparence black nature electric conduction film of the two-layer structure of this invention will be obtained.

[0033] Since the particles of conductive metal impalpable powder contact directly by this 2nd approach, without making a silica intervene in between in order to coat-ize powder in the condition that there is no binder in the beginning, electronic path structure is easy to be formed and it is effective in the reduction in resistance. Moreover, since the printing process which time amount and energy cost require can be managed at once, a production process is simplified.

[0034] The 1st approach: By the 1st approach, the coating used for formation of a lower layer conductive layer is prepared by making the solution of alkoxysilane distribute metal impalpable powder and black powder. The common use means generally used for manufacture of a coating can attain distribution of this powder. The amount of alkoxysilane is SiO2 conversion and is the total quantity 100 of metal impalpable powder and black powder. Within the limits of 1 - 18 weight section is desirable to the weight section.

[0035] Although it will not be restricted especially if a solvent can dissolve alkoxysilane, a desirable solvent is an alcoholic solvent which consists of a mixed solvent with one sort or two sorts or more of alcohol or alcohol, other compatibility organic solvents and/, or water. As alcohol, alkoxy alcohol, such as 2-methoxyethanol besides monohydric alcohol, such as a methanol, ethanol, isopropanol, a butanol, and a hexanol, is also independent, or it can be used, mixing with monohydric alcohol.

[0036] It can be made to be able to hydrolyze beforehand and alkoxysilane can also be used for a coating. Thereby, printing after spreading can be made to complete for a short time. The hydrolysis in this case is an acid catalyst in order to promote a reaction. (organic acids, such as inorganic acids, such as an example and a hydrochloric acid, or p-toluenesulfonic acid) It is desirable to carry out under existence of water. Being able to perform hydrolysis of alkoxysilane under a room temperature thru/or heating, desirable reaction temperature is within the limits of 20-80 degrees C.

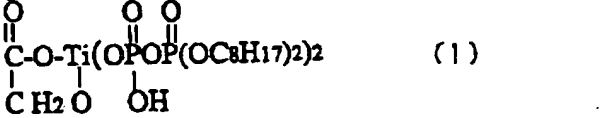
[0037] If it is in a suitable mode, this coating is alkoxy titanium further. (this may also be hydrolyzate) And at least one sort of titanium compounds chosen from the group which consists of a titanium coupling agent are contained. Effectiveness is to secure low resistance-ization which this titanium compound acted as a film reinforcing agent, equalized the affinity between the particles of the metal impalpable powder in a lower layer conductive layer, and black powder, and was excellent in the stable repeatability.

[0038] the case where this is used for this titanium compound -- the total quantity of metal impalpable powder and black powder -- receiving -- 0.1 - 5 % of the weight -- desirable -- It is good to use it in 0.2 - 2% of the weight of an amount. 0.1 Under by weight %, if the above-mentioned effectiveness cannot be acquired but it exceeds 5 % of the weight, the electronic pass between powder particles will be checked and conductivity will fall.

[0039] As an example of the alkoxy titanium which can be used by this invention, they are tetraisopropoxy titanium and tetrakis (2-ethyl HEKISOKISHI). Tetra-alkoxy titanium, such as titanium and tetra stearoxy titanium, and JIISO propoxy screw (acetylacetonate) Titanium, G n-butoxy screw (triethanol AMINATO) Titanium, dihydroxy screw (RAKUTATO) Tori, such as titanium and titanium-i-propoxy octylene glycolate, JI, or mono-alkoxy titanium is mentioned. Tetra-alkoxy titanium is desirable. Alkoxy titanium can also be used as the hydrolyzate. Hydrolysis of alkoxy titanium can be carried out like hydrolysis of alkoxysilane.

[0040] On the other hand for the example of a titanium coupling agent, isopropylisostearoyl titanate, Isopropyl tridecyl benzenesulphonyl titanate, isopropyl tris (dioctylpyrophosphate) Titanate, Tetra-isopropyl screw (dioctyl phosphite) Titanate, Tetra-octyl screw (JITORIDE sill phosphite) Titanate, Tetrapod (2 and 2-diaryl oxymethyl-1-butyl) screw (G tridecyl) Phosphite titanate, screw (dioctylpyrophosphate) Oxy-acetate titanate and tris (dioctylpyrophosphate) There is ethylene titanate etc. A desirable titanium coupling agent is the following structure expression. (1) - (8) It is shown.

[0041]
[Formula 1]



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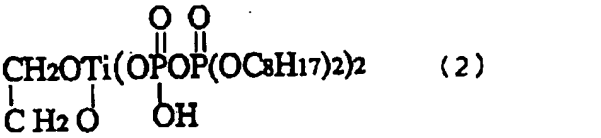

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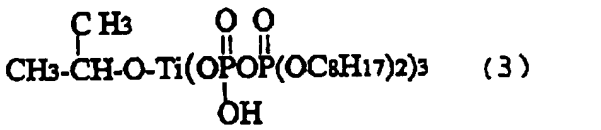

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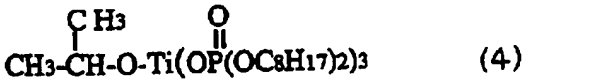

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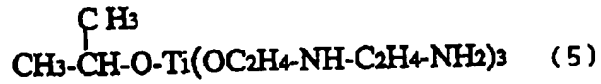

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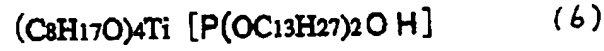

(6)

(7)

(8)

[0042] this lower layer coating for conductive layer formation -- a request -- various kinds of additives which can be added in coatings -- one sort -- or two or more sorts may be contained further. As such an additive, it is a surface active agent especially effective in the improvement in dispersibility of black powder. (a cation system, an anion system, Nonion system) There is an acid for promoting hydrolysis of alkoxysilane etc.
[0043] A lower layer conductive layer is 1000 nm so that it may mention later. Since the following thin films are enough, a coating is diluted if needed so that it may become the viscosity which is easily obtained by the applying method which this thin film adopted. general -- viscosity of the coating of this invention 0.8 - 10 cps -- especially -- 0.9-5cps The range is desirable.
[0044] Although spreading of a coating can be performed by the spray method, the spin coat method, dip coating, etc., the point of membrane formation precision to a spin coat method is the most desirable. As for spreading, it is desirable 20 - 1000 nm and to carry out after desiccation, so that the lower layer conductive layer of the thickness of the range of 30 - 600 nm may be formed especially. Thickness is 20 nm. In the following, neither conductivity nor low reflexibility can fully be given, but it is 1000 nm. It is membranous transparency when it becomes thick. (light permeability) When spoiled, a crack etc. is produced, adhesion falls, and the film becomes easy to separate.
[0045] Especially printing after spreading is preferably performed below 250 ** 200 ** and by heating below to 180 ** still more preferably for omission prevention of the dimensional accuracy of the Braun tube and a fluorescent substance, when a transparence base is the Braun tube. When transparence bases are things other than the Braun tube, a drying temperature higher than this may be adopted within limits which the base quality of the material is allowed.
[0046] In this way, the upper layer of the quality of a silica is formed on the formed lower layer conductive layer which contains metal impalpable powder and black powder in the nature matrix of a silica. The coating for the upper formation is easy to be what was constituted from a solution of

alkoxysilane or its hydrolyzate, and in order to promote hydrolysis of the alkoxysilane after spreading, it may carry out little addition of the acid at a coating. It is more desirable to use the hydrolyzate of alkoxysilane, in order to make viscosity high, since the coating for the upper layers does not contain powder. The desirable viscosity of this coating is 1 - 5 cps. The class of a solvent or acid, the method of application, and the printing temperature after spreading are the same as that of the thing explaining the coating for lower layer formation, and are good.

[0047] The upper coat of the quality of a silica which does not contain powder has a low refractive index compared with a lower layer, and, thereby, the two-layer film of low reflexibility as well as the conventional conductive two-layer film is obtained. The thickness of the upper coat desirable to this function is 20 - 150 nm, especially 50 - 120 nm.

[0048] The 2nd approach: By the 2nd approach, the coating used for formation of a lower layer conductive layer does not contain the alkoxysilane which functions as a binder. That is, the coating prepared by making a solvent [****] distribute metal impalpable powder and black powder is used.

[0049] The solvent to be used is good at one sort or two sorts or more of solvents which it was not restricted especially when metal impalpable powder and black powder could be distributed, but were chosen from an organic solvent and water. As an example of an usable organic solvent, sulfoxides, such as amides, such as hydrocarbons, such as ketones, such as alcohols, such as a methanol, ethanol, isopropanol, a butanol, and a hexanol, an acetone, a methyl ethyl ketone, methyl isobutyl ketone, a cyclohexanone, an isophorone, and 4-hydroxy-4-methyl-2-pentanone, toluene, a xylene, a hexane, and a cyclohexane, N.N-dimethylformamide, and N,N-dimethylacetamide, and dimethyl sulfoxide, are mentioned.

[0050] Also with the 2nd approach, a desirable solvent is an alcoholic solvent, i.e., one sort, or two sorts or more of alcohol or alcohol, and other organic solvents. (the above-mentioned ketone solvent is desirable) And/or, it is the mixed solvent which mixed water.

[0051] It is desirable to make a solvent, especially an alcoholic solvent contain at least one sort of alkoxy ethanol or beta-diketone. Alkoxy ethanol and beta-diketone have the operation which strengthens association between conductive impalpable powder particles, and raise the membrane formation nature of the coating which does not contain the binder for lower layer conductive layer formation. By that cause, membrane formation precision improves, a front face becomes smoother, and the lower layer conductive layer to which the haze and the reflection factor fell is obtained.

[0052] As an example of alkoxy ethanol, it is 2-methoxyethanol and 2. - (methoxyethoxy) Ethanol, 2-ethoxyethanol, 2 - (n-, iso-) Propoxy ethanol, 2 - (n-, iso-, tert-) Butoxy ethanol, 1-methoxy-2-propanol, 1-ethoxy-2-propanol, 1-(n-, iso-) propoxy-2-propanol, 2-methoxy-2-propanol, 2-ethoxy-2-propanol, etc. are mentioned. For the example of beta-diketone 2, 4-2,4-pentanedione (= acetylacetone) There are the 3-methyl -2, 4-2,4-pentanedione, 3-isopropanal pull -2, 4-2,4-pentanedione, 2, and 2-dimethyl -3, 5-hexane dione, etc. As beta-diketone, an acetylacetone is desirable.

[0053] As explained also by the 1st approach, the coating for lower layer conductive layer formation is alkoxy titanium as a film reinforcing agent in addition to a solvent and the two above-mentioned kinds of powder. (the hydrolyzate is sufficient) And it is desirable to contain at least one sort of titanium compounds chosen from the titanium coupling agent. The class and addition of this titanium compound are as having explained the 1st approach.

[0054] This coating may contain the addition component of further others. In the example of this addition component, it is a surface active agent. (a cation system, an anion system, Nonion system) pH regulator (amines, such as an organic acid or an inorganic acid, for example, a formic acid, an acetic acid, a propionic acid, butanoic acid, octylic acid, a hydrochloric acid, a nitric acid, and perchloric acid) There is a small amount of organic resin etc.

[0055] the viscosity of this coating -- desirable -- 0.8 - 10 cps -- more -- desirable -- It is 0.5 - 5 cps. for holding the distributed stability of metal impalpable powder and black powder distributed in the coating good -- liquid pH 4.0-10 -- especially -- 5.0-8.5 It is desirable that it is within the limits.

[0056] The thickness of the lower layer coat which consists of the method of application of this coating and two kinds of powder formed is the same as that of the 1st approach, and is good. Since the coating does not contain the binder, the thickness of the powder coat formed from this coating is dependent on the sum density of the metal impalpable powder and the black powder in a coating. therefore -- although what is necessary is just to choose this sum density according to the method of application to be used so

that the lower layer coat of predetermined thickness may be formed -- usually -- 0.5 - 20% of the weight of within the limits -- it is -- desirable -- It is 1.0 - 5% of the weight of within the limits.
[0057] After applying to a base front face the coating which does not contain the alkoxysilane for lower layer conductive layer formation, a solvent is suitably evaporated with a means and the coat which consists of the two above-mentioned kinds of powder substantially is formed on a base. Evaporation of this solvent can be carried out with no heating or heating according to the boiling point of the used solvent. For example, if it fully takes turnover time although based also on the class of solvent in applying with a spin coat method, a solvent can be evaporated during rotation, without heating. In addition, evaporation of a solvent did not need to be performed completely and a part of solvent may remain.
[0058] Then, the coating for the upper formation is applied. This coating consists of a solution of alkoxysilane or its hydrolyzate like the 1st approach, and the solvent to be used is the same as that of the coating used for the 1st approach, and is good. By the 2nd approach, when the coating for the upper formation permeates the gap between the particles of a lower layer powder coat and bakes the upper layer and a lower layer at once after spreading of this coating, the lower layer conductive layer of a high refractive index with which powder was closely combined by the silica is formed. On the other hand, since the upper coating which did not permeate a lower layer forms the upper layer of the quality of a silica of a low refractive index which covers this conductive layer, the low reflexibility made into the purpose is secured. By request, additives, such as a surfactant for adjustment of permeability, can be added in these coatings.
[0059] Since printing of a lower layer and the upper layer is carried out at once, in order to promote hydrolysis of the alkoxysilane under printing by the 2nd approach, it is desirable to use alkoxysilane as hydrolyzate and it is desirable to use the thing in the condition of being called especially a silica sol. A silica sol is an acid catalyst about alkoxysilane. (preferably a hydrochloric acid or a nitric acid) It can prepare by making it hydrolyze under a room temperature or heating under existence.
[0060] When using a silica sol, the silica sol concentration in the coating for the upper formation is SiO2 conversion. 0.5-2.5 Within the limits of weight % is desirable. the viscosity of this coating -- desirable -- 0.8 - 10 cps -- more -- desirable -- 1.0 - 4.0 cps it is . If silica sol concentration is too low, association of lower layer powder and the upper thickness will become inadequate, if too high, membrane formation precision will fall and control of the upper thickness will become difficult. Moreover, if the viscosity of this coating is too high, when a silica sol will not fully sink into the gap between lower layer powder particles and conductivity will fall, membrane formation precision falls, and control of the upper thickness also becomes difficult. The upper method of application, thickness, and the printing temperature after spreading are the same as that of the 1st approach, and are good. By the 2nd approach, although spreading of a coating is performed twice, if it applies with a spin coat method, since it can apply continuously and will burn at once after that by dropping the coating for lower layers, and the coating for the upper layers in order on one set of a spin coater, it can carry out by the same simple routing as one spreading substantially.
[0061] As a result of investigating the cross section of the thickness direction of the transparence black nature electric conduction film of the two-layer membrane structure of this invention formed by the 2nd approach, it became clear that the content of the powder in a lower layer conductive layer increased gently from an interface with the upper layer rather than that shows rapid increase. On the other hand, when it forms by the 1st approach, the content of lower layer conductive powder increases rapidly from an interface with the upper layer.
[0062] There is the description that little fluctuation of the light minimum reflection factor when the direction of the two-layer membrane structure formed by the 2nd approach changing the thickness of a lower layer conductive layer is. That is, for a reflection factor, the value of a thickness (nm) x refractive index is lambda/4 (lambda is the wavelength <nm> of an incident ray). When equal, it becomes the minimum, but by the two-layer film formed by the 2nd approach, even if lower layer thickness separates greatly from this value, the light minimum reflection factor can be kept low. On the other hand, the 1st approach has the description that control of the thickness for each class is easy, and the thickness of the upper layer and a lower layer can be easily controlled so that the light minimum reflection factor becomes the lowest.
[0063] Even if it forms by which approach, the transparence black nature electric conduction film of the

two-layer structure of this invention holds the transparency which wore the black taste by low resistance, and has the optical description of low reflexibility. The conductivity of this transparence black nature electric conduction film is the class and loadings of the metal impalpable powder in a lower layer. (black powder comparatively) It responds, and changes sharply and, generally membranous surface electrical resistance is 100. It changes within the limits of omega / ** base to 105ohms / ** base. Therefore, what is necessary is just to choose the class and loadings of metal impalpable powder according to electromagnetic wave shielding extent demanded. the case where ITO powder is used as conductive powder -- 103 using metal impalpable powder by this invention, since the surface electrical resistance of omega / ** base came out at most and there was -- further -- conductivity -- 100 It can raise to the surface electrical resistance of omega / ** base.

[0064] Moreover, since the transparence black nature electric conduction film of this invention contains black powder in a lower layer conductive layer, blue like the conventional two-layer film - purplish, or the red - yellow taste is canceled, and it is colorlessness substantially. Although the lower layer contains metal impalpable powder and black powder densely, since the haze holds sufficient transparency for practical use of 60% or more in less than 1% and total light transmission and this electric conduction film has the silica layer of a low refractive index in the upper layer, it can show the low light minimum reflection factor of less than 1%. Moreover, the contrast of an image can be raised by wearing the black taste.

[0065]

[Example]

(Example 1) In this example, the transparence black nature electric conduction film of two-layer structure was formed on the glass base by the 2nd approach mentioned above.

[0066] To the mixed solvent of the weight ratios 80/20 of the coating isopropanol / 2-iso-propoxy ethanol for lower layer formation It adds at the class shown in Table 1, and a rate with the titanium compound of the class which shows metal impalpable powder and black powder in Table 1 by the case, and an amount. By mixing with a paint shaker using the zirconia beads of diameter 0.3 mm, two kinds of powder was distributed in the solvent, and the coating for lower layer formation which does not contain alkoxysilane was prepared. For each the metal impalpable powder and the black powder in this coating, the first [an average of] particle diameter is 0.1. It is below mum and a coating totals two kinds of this powder. 0.7-3.2 It contains in the amount of weight % and is the viscosity of a coating. 1.0-1.6cps It was within the limits.

[0067] The semantics of the notation of the titanium compound used for Table 1 is as follows.
a: Isopropyl tris (dioctylpyrophosphate) Titanate [Compound of the above-mentioned structure expression (3)] b: Tetrapod (2 and 2-diaryl oxymethyl-1-butyl) Screw (G tridecyl) Phosphite titanate [Compound of the above-mentioned structure expression (8)] c: Screw (dioctylpyrophosphate) Oxy-acetate titanate [Compound of the above-mentioned structure expression (1)] .

[0068] It replaced with metal impalpable powder for the comparison, and the coating containing following ITO powder or following ATO powder was prepared similarly.
ITO powder: Amount % and the first [an average of] particle diameter of 0.02 micrometers of Sn dopes of five mols, the amount first [an average of] particle diameter of 0.02 micrometers of ATO powder:Sb dopes of five mols. [%,]

[0069] Coating ethoxy silane for the upper formation (ethyl silicate) Heat at 60 degrees C for 1 hour, they was made to hydrolyze in the ethanol containing a little hydrochloric acid and water, and the silica sol was compounded. The obtained silica sol solution was diluted with the mixed solvent of the weight ratio 5:8:1 of ethanol / isopropanol / butanol, SiO2 conversion concentration prepared and viscosity prepared the coating of 1.65 cps 0.70% of the weight.

[0070] soda lime glass of a dimension with a membrane formation approach 100 mmx100 mmx thickness of 3mm (blue plate glass) from -- the spin coater was used for one side of the becoming base, and the coating for lower layer formation and the coating for the upper formation were dropped in order, and membranes were formed. For each coating, a drip is 5-10g, and a rotational frequency. 140 - 180 rpm and turnover time are 60-180. It was within the limits of a second. Then, the base was heated for 30 minutes in atmospheric air at 170 **, the paint film was baked, and the transparence black nature electric conduction film was formed on the glass base. The property of the obtained film was evaluated as follows.

[0071] Evaluation thickness of a film property: The thickness of each class was measured by the SEM cross section.
Surface electrical resistance: Four point probe method (RORESUTA AP: Mitsubishi Petrochemical make) It measured.
Light transmittance (total visible-ray permeability) : recording spectrophotometer (U-4000 mold: Hitachi make) It measured.
Haze: Hazemeter (HGM-3D: Suga Test Instruments make) It measured.
[0072] The light minimum reflection factor: To the tooth back of a glass base, it is a black vinyl tape. (No.21: NITTO DENKO) It stuck, and after keeping it warm at 50 degrees C for 30 minutes and forming a black mask, the reflectance spectrum of the visible region wavelength by 12-degree specular reflection was measured with the recording spectrophotometer. This reflectance spectrum to visibility is high. The minimum value of the reflection factor in 500 - 600 nm was calculated, and this was made into the minimum reflection factor.
[0073] The above test result is also collectively shown in Table 1. Moreover, trial No.7 Transparence black nature electric conduction film of the example of this invention (Ag impalpable powder and black-titanium-oxide powder are contained) It is drawing 1 (a) about a transparency spectrum and a reflectance spectrum. And (b) Trial No.13 Transparence black nature electric conduction film of the example of a comparison (ITO powder and black-titanium-oxide powder are contained) It is drawing 2 (a) about a transparency spectrum and a reflectance spectrum. And (b) It is shown.
[0074]
[Table 1]

区分	試験No.	下層形成用塗料の組成（部は重量部、残部は溶媒） 金属微粉末 種類	部	黒色粉末 種類[1]	部	粉末合計wt%	チタン化合物 種類	wt%[2]	膜厚（nm） 下層 導電層	上層 シリカ層	膜特性 表面抵抗（Ω／□）	光透過率（%）	ヘーズ（%）	最低反射率（%）
本発明例	1	Cu	95	$TiO_{0.88}N_{0.04}$	5	2.8	a	1.0	530	85	1.5×10^{3}	75.5	0.6	0.98
	2	Cu－Ag[3]	85	〃	15	3.1	なし	—	600	65	7.0×10^{2}	68.8	0.7	0.95
	3	Ni	77	〃	23	3.2	b	2.0	220	70	5.5×10^{3}	69.5	0.8	0.91
	4	Ni－Ag[4]	80	〃	20	1.8	なし	—	280	75	8.5×10^{2}	60.8	0.7	0.93
	5	W／Ag[5]	85	$TiO_{1.2}N_{0.08}$	15	2.2	なし	—	210	80	1.0×10^{3}	63.3	0.6	0.90
	6	Ag-Pd/ATO[6]	20	〃	80	2.0	c	0.1	70	95	2.1×10^{4}	81.1	0.4	0.76
	7	Ag	80	$TiO_{1.05}N_{0.04}$	20	2.4	c	0.1	92	105	1.3×10^{0}	68.8	0.3	0.68
	8	Ag	65	〃	35	1.4	なし	—	84	95	3.5×10^{3}	80.5	0.3	0.78
	9	Ag	83	マグネタイト	17	1.6	なし	—	68	90	7.5×10^{2}	71.8	0.4	0.71
	10	Ag	70	カーボンブラック	30	1.8	なし	—	105	85	6.6×10^{2}	70.1	0.3	0.77
	11	Au-Pd[7]	5	$TiO_{1.2}N_{0.08}$	95	0.7	なし	—	65	90	6.1×10^{5}	77.8	0.3	0.85
比較例	12	ITO	100	なし	—	1.7	なし	—	95	90	9.8×10^{3}	96.8	0.1	0.81
	13	ITO	85	$TiO_{1.08}N_{0.11}$	15	2.2	なし	—	80	85	5.5×10^{4}	97.0	0.2	0.77
	14	ATO	88	〃	12	2.0	なし	—	110	90	7.6×10^{6}	86.7	0.3	0.89

（注） 1：チタンブラックは TiO_xN_y の組成で示す；　2：金属微粉末と黒色粉末の合計量に対する重量%；
3：Cu-45wt%Ag合金；　4：Ni-68wt%Ag合金；　5：W28wt%とAg72wt% との混合粉末；
6：Ag-60wt%Pd合金70wt% とATO30wt% との混合粉末、　7：Au-20%Pd合金

[0075] as shown in Table 1, in the example of this invention, the thickness of a lower layer conductive layer is migrating to the large range of about 65 to 600 nm (it may separate greatly from lambda/4) irrespective of -- 1% or less of the light minimum reflection factor, 1% or less of haze, and 60% or more of total visible-ray permeability are shown, and, as for the obtained electric conduction film, it turns out that it is the film of low reflexibility excellent in visibility. Moreover, membranous surface electrical resistance is 100 as be comparatively alike in the class and black powder of metal impalpable powder. omega / ** base to 105 It changed to the large area to omega / ** base. That is, it is required to be able to change membranous conductivity according to electromagnetic wave shielding [which is demanded], and fill electromagnetic wave shielding [severe]. 100-101 It turns out that the transparence black nature electric conduction film with the surface electrical resistance of omega / ** base of very low resistance can also be obtained.

[0076] On the other hand, although transparency becomes high when ITO powder is used as conductive powder, conductivity is at most 103. It is as low as the surface electrical resistance of omega / ** base, and it turns out that a severe electromagnetic wave shielding demand cannot be filled. When ATO powder is used, surface electrical resistance is 106. Even if it is very as high as omega / ** base and antistatic ability can be given, it cannot demonstrate electromagnetic wave shielding.
[0077] Drawing 1 (a) Transparence black nature electric conduction film of the shown example of this invention (conductive powder is Ag powder) Since permeability is stopped around about 65% almost uniformly in the whole visible region, a transparency spectrum shows that the film wears the black taste. Moreover, drawing 1 (b) It is drawing 2 (b) about the reflectance spectrum of this shown transparence black nature electric conduction film. Shown example of a comparison (conductive powder is ITO powder) As compared with a reflectance spectrum, the electric conduction film of the example of this invention of 400 nm of a visible region end and the reflection factor near 800 nm is lower than the example of a comparison, and it turns out that the improvement effectiveness of the visibility by low reflexibility becomes rather larger than the case where ITO powder is used.
[0078] (Example 2) In this example, the transparence black nature electric conduction film of two-layer structure was formed on the glass base by the 1st approach mentioned above.
[0079] It is a tetra-ethoxy silane as a coating binder for lower layer formation. (ethyl silicate) The total quantity 100 of metal impalpable powder and black powder It was the same as that of an example 1 except having added at a rate of 10 weight sections per weight section and by SiO2 conversion, and having added still a small amount of hydrochloric acid as a hydrolysis catalyst.
[0080] It was the same as that of the coating example 1 for the upper formation.
After applying the coating for lower layer formation on a base by the membrane formation approach spin coater, before applying the coating for the upper formation by the spin coater, it was the same as that of an example 1 except having heated for 5 minutes at 50 degrees C among atmospheric air, and having carried out lower layer printing.
[0081] The membrane structure and the test result of black conductivity impalpable powder of two-layer structure which were obtained are collectively shown in Table 2. Table 2 shows that the transparence black nature electric conduction film with the property same with having formed membranes by the 2nd approach shown in the example 1 also by the 1st approach is obtained.
[0082]
[Table 2]

区分	試験No.	下層形成用塗料の組成（部は重量部、残部は溶媒）								膜厚(nm)		膜特性			
		金属微粉末		黒色粉末		粉末合計 wt%	エチルシリケート wt%[2]	チタン化合物		下層 導電層	上層 シリカ層	表面抵抗 (Ω/□)	光透過率 (%)	ヘーズ (%)	最低反射率 (%)
		種類	部	種類[1]	部			種類	wt%[3]						
本発明例	1	Ag	80	$TiO_{1.05}N_{0.04}$	20	1.4	0.14	なし	—	54	85	1.8×10^{3}	61.2	0.7	0.51
	2	Ag	85	カーボンブラック	15	1.6	0.16	c	0.10	68	80	8.6×10^{2}	60.8	0.4	0.38
	3	Ag	90	$TiO_{0.88}N_{0.04}$	10	1.0	0.10	なし	—	52	82	2.0×10^{3}	64.1	0.6	0.39

(注) 1：チタンブラックは TiO_xN_y の組成で示す； 2：SiO_2換算wt%； 3：金属微粉末と黒色粉末の合計量に対する重量%。

[0083]
[Effect of the Invention] The transparence black nature electric conduction film of this invention is 100 by the class and loadings of metal impalpable powder which are used as conductive powder. omega / ** base to 105 It has a wide range surface-electrical-resistance value to omega / ** base, conductivity can be adjusted according to the electromagnetic wave shielding level demanded, and the severe electromagnetic wave shielding demand can also be met.
[0084] Moreover, in spite of this transparence black nature electric conduction film's not having the reflected light of the purple which had become a problem conventionally - blueness, or the red - yellow taste and containing metal impalpable powder, the light minimum reflection factor is equipped with the low reflexibility and sufficient transparency preferably of [haze / 60% or more] 70% or more in 1% or less and total visible-ray permeability below 1 %. Therefore, while it can prevent reflected [the external image by reflection] by forming the transparence black nature electric conduction film of this invention in the glass front face of the front panel of the Braun tube, it can give electromagnetic wave shielding

[which can prevent certainly leakage of the electromagnetic wave which poses a problem especially with CRT for personal computers, and the Braun tube for large-sized TV / advanced] to the Braun tube. Moreover, since the film wears the black taste, the contrast of an image improves.

[0085] Therefore, the transparence black nature electric conduction film of this invention not only makes an image legible by improvement in the visibility of the Braun tube, and contrast, but is useful also to the bad influence to the body and the prevention of KOMPYUTA malfunction by leakage of an electromagnetic wave.

[Translation done.]

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1.This document has been translated by computer. So the translation may not reflect the original precisely.
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CLAIMS

[Claim(s)]
[Claim 1] Transparence black nature electric conduction film equipped with low reflexibility, quantity KONSUTO last nature, and electromagnetic wave shielding which consists of a lower layer which contains metal impalpable powder and black powder in the nature matrix of a silica prepared in the front face of a transparence base, and the upper layer of the quality of a silica prepared on it.
[Claim 2] Transparence black nature electric conduction film according to claim 1 whose black powder is black titanium oxide.
[Claim 3] Transparence black nature electric conduction film according to claim 1 or 2 whose transparence base is the front panel of the Braun tube.
[Claim 4] Metal impalpable powder Fe, Co, nickel, Cr, W, aluminum, In, Zn, Pb, One sort or two sorts or more of metals chosen from the group which consists of Sb, Bi, Sn, Ce, Cd, Pd, Cu, Pt, Ag, and Au, And transparence black nature electric conduction film given in claim 1 thru/or any 1 term of 3 which consists of mixture of/or the alloy of these metals and/or these metals and/, or an alloy.
[Claim 5] the total quantity of metal impalpable powder and black powder -- receiving -- 5 - 97 % of the weight -- comparatively -- coming out -- metal impalpable powder -- containing -- lower layer thickness -- 20 - 1000 nm it is -- transparence black nature electric conduction film given in claim 1 thru/or any 1 term of 4.
[Claim 6] The total quantity of metal impalpable powder and black powder is received in at least one sort of titanium compounds chosen from the group which a lower layer becomes from alkoxy titanium, its hydrolyzate, and a titanium coupling agent in addition to metal impalpable powder and black powder. Transparence black nature electric conduction film given in claim 1 thru/or any 1 term of 5 characterized by being formed from the coating contained in 0.1 - 5% of the weight of an amount.

[Translation done.]